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Anionic Polymerization
to
Cationic Polymerization

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General References

Refs. 1-3 give general information on the properties and reactions of ions in solution, including chapters on polymerization.
 Refs. 4-10 are books or longer review articles specifically on anionic polymerization. Refs. 5 and 10 are largely concerned with anionic polymerization mechanisms; Ref. 8 is a valuable record of the state of the art in 1980. Most of the research workers active in the field contributed to this symposium.

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ANNEALING

The annealing of plastics can be defined as a secondary process wherein the plastic is brought to a certain temperature, kept there for a time, and then cooled to room temperature. The primary reasons for annealing include the reduction or removal of residual stresses and strains, dimensional stabilization, reduction or elimination of defects, and improvement of physical properties (1).

In the plastics industry, annealing has been applied primarily to thermoplastic polymers, block copolymers, and amorphous or semicrystalline polymer blends (2-56).

Although the main effect of annealing is to increase the density of the plastic, recent work indicates that other changes occur as well (57-64). The annealing of semicrystalline polymers may change the crystal structure, the degree of crystallinity, the perfection of the crystals, and the orientation of both the crystalline and amorphous material (2-22).

The annealing of polymer blends (qv) and block copolymers (qv) may result in enhanced phase and microphase separation, and may also change the surface

of the materials, making them more or less susceptible to stress crazing (qv) and stress cracking (23-39). The same problem may occur in amorphous and crystalline plastics.

In most cases, the induced stresses and orientation may be insignificant, and no annealing is required if proper processing conditions have been used during fabrication. However, annealing becomes necessary when the molded parts are excessively stressed, when maximum dimensional stability (qv) and heat resistance are required, or when certain properties must be enhanced. Improper annealing may also cause deterioration in performance.

Thermal Background

In all forming operations, such as injection molding (qv) or extrusion (qv), frozen-in orientation and residual stresses arise from two sources. The first is the flow-induced stresses (shear and normal), which occur during flow through restricted channels and lead to the orientation of the polymer chains; if these stresses do not completely relax during the subsequent cooling period, they appear as frozen-in birefringence and flow stresses in the plastic. In the case of injection molding, extensional flow of the melt front also causes birefringence. The second source is the differential density or shrinkage and the viscoelastic behavior of the plastic during nonuniform cooling through a glass-transition or a crystallization temperature, resulting in thermal stresses and birefringence. Recent work suggests that coupling between these various stresses occurs during cooling and annealing. The degree of coupling appears to depend upon molecular conformers and is not yet completely understood. The frozen-in strain pattern in injection-molded parts is more complex than in extruded film or sheet.

Stresses may be induced in polymeric glasses by cooling from above their glass transition. This is best understood by reference to the volume-temperature curves in Figure 1. If the polymer is cooled rapidly from temperature T^* to some temperature T_1 , then its outer surface is transformed to a rigid glass while the core is still above its glass transition. The result is differential contraction between the outer surface and the core because of their different thermal coefficients of expansion. The volume-temperature behavior of the skin is represented by the line ABC in Figure 1. Since the surface is restrained from shrinking by the core, it is in a state of tension. The core cools more slowly and follows the line ADE. During this cooling period, skin and core undergo a reduction in volume accompanied by changes in the stress profiles.

Inasmuch as the core ultimately shrinks more than the skin, the resultant stress profile is inverted, as shown by curve A in Figure 2, i.e., the skin is in a state of compression and the core in a state of tension. If high packing pressures are required to fill the mold, when the part is removed, it swells and the residual stress profile shifts to that shown by curve B.

It is well known that during injection molding a solid layer is formed when the polymer melt front reaches the mold wall. The thickness of this layer is determined by the mold, the melt temperature, the mold temperatures, and the flow rate. The remaining space in the mold is subsequently filled by passage of the melt through this outer layer. These layers, in contrast to the core, are

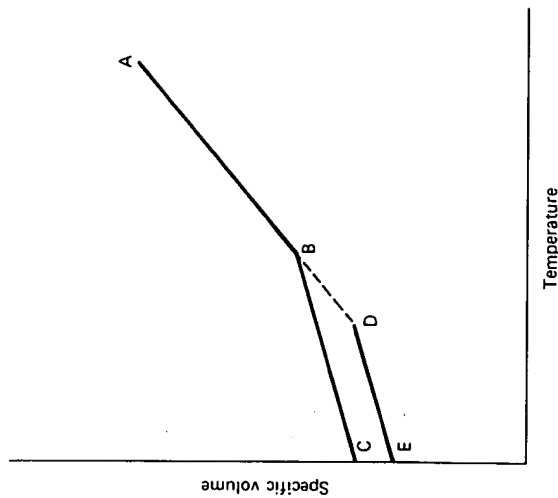


Fig. 1. Hypothetical curves for the specific volume-temperature behavior of fast and slowly cooled amorphous plastics. ABC = fast cooling; ADE = slow cooling.)

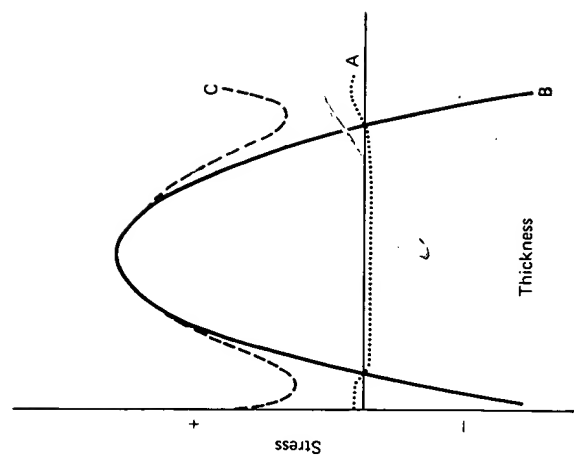


Fig. 2. Curve A shows the expected stress distribution through the thickness of an amorphous thermoplastic after the surface has been quenched below its glass transition, while the core is still above its glass transition; curve B depicts the new stress distribution through the thickness of the sample described after the entire sample has been cooled below its glass transition and has reached equilibrium; curve C depicts the stress distribution through the thickness of an amorphous thermoplastic that was molded at an elevated packing pressure, cooled below its glass transition, and removed from the mold.

quenched in position and do not have time to undergo significant relaxation (see also MOLDS).

From several detailed studies, an expression for the expected residual stress profile has been derived using the method of finite elements:

$$\Delta\sigma_i = \left(\frac{1}{1 - \mu} \right) [(\alpha_i \Delta T_i + \Delta\epsilon E_i - \Delta\sigma_i \text{vol})] - \Delta P$$

where i denotes the i th section, α the thermal coefficient of expansion, μ Poisson's ratio, E the elastic modulus (stress relaxation), $\Delta\sigma$ the residual stress, and $\Delta\epsilon$ the shrinkage (65). The first term in square brackets describes the stresses caused by the thermal gradient, and the second, the stress relaxation. The last term, ΔP , is the hydrostatic stress that the plastic is exposed to during molding and before the opening of the mold. Under normal molding conditions, ie, low pressures and high temperatures, the residual stresses are compressive at the surface and tensile in the interior. High molding pressures and longer holding times can lead to an inversion of the stress profile, ie, tensile at the surface and compressive in the interior. More complicated profiles have been observed, but they are not understood.

In the case of semicrystalline polymers, densification results from crystallization and, as in the case of the glassy polymers, changes occurring in the skin and in the core cause stresses. However, the situation is more complex because of the different mechanisms of crystallization, ie, row nucleation, and the fact that secondary crystallization may occur minutes, hours, or days later (2-23).

In the case of polymer blends and block copolymers, densification may be the result of phase separation, microphase separation, crystallization, or simple glass formation. Such materials obviously exhibit more complex behavior because of these different densification modes, which can be affected by fabrication conditions and the thickness and geometry of the part and the plastic (24-31).

In forming parts by injection molding, variations in part thickness can enhance shear stresses and pressure differentials that may cause internal flow (66).

Vacuum thermoforming and other thermoforming (qv) procedures can lead to orientation and thermal stresses. Internal stresses are also introduced during the machining (qv) of molded parts, ie, during cutting, drilling, and sawing. Stresses may also be introduced when parts are welded by a linear vibration process or bonded by strong adhesives. These stresses act like the frozen-in stresses set up during forming operations (see BONDING in ADHESION AND BONDING).

Failure M d s

Molded thermoplastics containing residual stresses and frozen-in orientation undergo stress crazing or stress cracking when placed in the wrong environment or momentarily exposed to certain liquids; these conditions represent the primary modes of plastics failure. Systematic studies of the morphology of crazes by various experimental techniques indicate that they are composed of drawn fibrils and voids (a foam structure) with dimensions on the order of 10-20 nm (see MICROMECHANICAL MEASUREMENTS). It has also been shown that the

stress-strain behavior of crazes is elastoplastic and that crazes precede brittle failure (66). Empirical correlations of the tendency toward crazing have been suggested, and it appears that this phenomenon is a reflection of the glass transition of the plastic, its yield stress, and its cohesive energy density (67).

In contrast to stress crazing, stress cracking seems to be related to the onset of crystallization within amorphous materials or to changes between contiguous crystalline phases. Thermooxidative and photolytic scission of tie chains between crystalline components can also result in stress cracking.

Principles

Initially, annealing of plastics was of industrial interest, but it has recently become of serious concern to scientists and engineers in academic and government laboratories, and has been named physical aging (1,61,62) (see AGING, PHYSICAL). Although the work has focused on the behavior of glasses, it increases understanding of the behavior of semicrystalline polymers, block copolymers, and polymer blends because of the development of new experimental techniques to monitor the changes.

For example, Fourier-transform infrared has been used to monitor the conformer population in poly(ethylene terephthalate) (PET) during annealing, and it was observed that the percentage of the gauche population changes dramatically, but the amount of trans isomer remains essentially constant. Correspondingly, solid-state nmr on PET indicates that the motion of methylene groups becomes more restricted upon annealing (60). Volumetric, mechanical, calorimetric, and optical methods have been used to monitor structural relaxation processes. Poly(vinyl acetate), poly(methyl methacrylate), bisphenol A polycarbonate, poly(ethylene terephthalate), and poly(vinyl chloride) have been studied by these techniques. New theories and models have emerged to explain the thermodynamics and the relaxation behavior of such systems. Although free volume, ie, the difference in volume of a glass at equilibrium and as received, had long been used to explain annealing, the newer theories invoke molecular conformers and their interactions with the local environment (68-78). Molecular modeling and computer simulation of the formation and aging of glasses have also been discussed, but differences exist between experiment and simulation.

The typical behavior of amorphous polymers, such as poly(vinyl acetate), polystyrene, poly(methyl methacrylate), and bisphenol A polycarbonate is shown in Figure 1. The upper curve (ABC), obtained by rapid cooling (quenching), results in a material of lower density than that obtained by slow cooling (ADE). The lower density of the quenched material was previously interpreted in terms of free volume, but is now associated with the freezing-in of higher energy states. As a result, the tendency of material to return to a lower energy state is impeded by the high viscosity of the polymer, 1 Pa-s (10 P). The glass transition of the quenched polymer is higher than that of the slowly cooled one.

There are two points of view with regard to the static and kinetic properties of glass-forming polymers. The first one, involving the concept known as free volume, has been used for several decades to interpret physical measurements. Several definitions of free volume have been proposed and are interconnected in

that all involve an excess volume. For example, free volume has been defined in terms of a van der Waals hard-sphere model, in terms of the fluctuations in volume and energy, in terms of mobility coefficients, and in terms of the volume differences of the glass and liquid or the glass and its crystal. The main reason for its acceptance have been its simplicity and utility in correlating large amounts of data.

A recent theory proposes that the underlying mechanisms reflect a single submolecular event, which couples with the local environment to yield a complex relaxation spectrum. This theory may provide a "molecular connection" to bulk phenomena, such as the formation and relaxation behavior of glasses. For example, parameters evaluated from dielectric data have been used to calculate the volumetric relaxation behavior of a glass (78). The interpretation of stress relaxation, creep (qv), and mechanical transitions has also been reported (61).

The annealing of semicrystalline plastics may change the degree of crystallinity, the size and orientation of the crystallites, their contiguous structural morphology, and number of tie chains between the crystallites (4).

When a semicrystalline polymer is cooled below its crystallization temperature, the onset of crystallization is controlled by the temperature interval below the melting point and the formation of critical nuclei or the presence of foreign nuclei (16).

Growth of the nuclei can occur by deposition of polymer chains on the nuclei surface, followed by folding into a structure like a fireman's hose or by a vertical alignment like a box of spaghetti. In either case, tie chains occur between the crystallites. For clean materials, the rates of nucleation and growth generally follow bell-shaped curves between the melting point and the glass transition of the polymer. The temperatures at which the maximum rates of nucleation and growth occur may be widely separated. For example, if poly(chlorotrifluoroethylene) or poly(butylene terephthalate) are thermally quenched from above their melt temperature T_m to below their glass transition T_g , nuclei are formed, but little, if any, crystallization occurs. Upon annealing, crystallites grow and the mechanical properties change significantly.

If nucleating agents have been added to the crystalline polymer, crystallization may occur just below the crystallization temperature, may be much faster, and may result in smaller crystallites more uniformly dispersed in the plastic, which tends to make the plastic zone flexible and more resistant to stress cracking (16). The nucleation and growth of new phases have been discussed in terms of the classical Flory-Huggins theory (62).

In many cases, the annealing of polymer blends and block copolymers involves the same principles discussed for glassy and crystalline polymers. However, polymer blends that undergo phase separation and block copolymers that undergo microphase separation are more complex, because the degree of phase separation and the morphology of the blends are affected by the processing conditions, the mode of separation, and, obviously, the annealing conditions (25,66).

Commercial polymer blends and block copolymers typically contain other low and intermediate molecular-weight additives, such as plasticizers, flame retardants, and uv and thermal stabilizers. During annealing, phase and microphase separation may be enhanced, and bleeding of the additives may be observed. The morphologies of polymer blends and block copolymers can be affected by

processing and quenching conditions. If the melt viscosities of the polymers are not matched, compositional layering perpendicular to the direction of flow may occur (66,67). As in the case of crystalline polymers, the skin may be different both in morphology and composition (64). Annealing may cause more significant changes in the skin than in the interior (4).

Equipment

The equipment used for annealing is similar to that used for preheating thermoplastic sheets, rods, or tubes before shaping. Depending on the annealing medium, ie, liquid or air, different heating units are used.

The equipment for liquid baths, ie, water, oils, or waxes, consists of tanks or troughs that should be of suitable size. To ensure uniform heating and maintain the required annealing temperature, a proper recirculating system and adequate temperature control should be provided. The temperature-control system should consist of a sensing element, a controller that interprets the information received from the sensing element, and a heating or cooling element regulated by the controller. Provision must be made for removing or recycling the liquid to prevent temperature build-up or localized hot spots.

When air is the heating medium, circulating-air or air-flow ovens have proved most suitable. An air-flow oven consists typically of two compartments: in one, the air is heated to the required temperature by gas or electricity, and in the other, the material is heated by hot air at the annealing temperature for the required time. To avoid dead spaces or hot spots, the hot air is rapidly circulated through the two compartments with compressors or blowers. If the temperature is carefully controlled in every part of the oven, the material can be left in the oven for a considerable time without undue deterioration.

The other methods of heating require convection ovens, infrared ovens, and dielectric heating devices. However, the air-flow ovens are preferable, despite their low heating rates. For the annealing of large shapings, air-flow ovens are almost essential, because the temperature must be uniform throughout. To secure uniform temperature, careful design of racks and ease of parts handling are very important. The clamping necessary for holding or suspending the parts in the oven should not exert too high a pressure, or deformation or distortion occurs during annealing.

A proper design should permit free air circulation to avoid formation of pockets of dead air where solvent vapors can accumulate. It should also provide for bleeding some air and admitting fresh air to permit air exchange. This prevents the accumulation of fumes and solvent vapors, if cemented parts are annealed.

After annealing, cooling must be very slow and gradual to avoid reintroducing stresses and thus defeating the purpose of annealing. Slow cooling is accomplished by immediately packing the parts in such a way as to provide adequate insulation or by allowing the parts to cool in the air oven or in a liquid bath with the heat turned off.

Occasionally, as in the case of films, annealing is done on hot rolls moving very slowly. This process is limited to minimum thicknesses of 3 mm, since thinner materials are distorted. In blown-film extrusion, the film is cooled by air

flowing through the annealing chamber (a tube placed between the die and the air ring). The cooling rate is controlled in such a way that the film surface can level out; rapid cooling preserves surface roughness developed during extrusion.

M thods

Theoretically, the most desirable annealing temperatures for amorphous plastics, some polymer blends, and block copolymers is above their glass transition, where the relaxation of stress and orientation is the most rapid. However, the required temperatures may cause excessive distortion and warping. To anneal as quickly as possible, the plastic is heated to the highest possible temperature at which dimensional changes owing to strain release are within permissible ranges. This temperature can be determined by placing the plastic part in an air oven or liquid bath and gradually raising the temperature by intervals of 3–5°C until the maximum allowable change in shape or dimension occurs. This distortion temperature is dictated by thermomechanical processing history, geometry, thickness, weight, and size. The annealing temperature should then be fixed about 5°C lower.

The time necessary for annealing at the distortion temperature varies with the thickness and geometry of the part, the annealing medium, and the degree of relief required. Optimum annealing conditions must be determined by experiment.

When a plastic part is annealed, volume changes depend upon the thermomechanical history, the annealing temperature and time, and the plastic's properties. In general, densification occurs, but may be preceded by a rarefaction.

If the specific volume-temperature curves for various thermal histories are available, the time and temperature necessary to produce a given density can be estimated from the relation

$$\frac{V_e - V}{V_e - V_i} = \exp - (kt) \left(\frac{1}{1 - n} \right)$$

where V_e is the equilibrium volume, V the starting volume, V_i the volume at time t , k a rate constant, and n a number between 0 and 1.

The annealing of crystalline polymers, polymer blends, and block copolymers may create changes in the degree of crystallinity or perfection of crystals and the degree of phase or microphase separation.

In these systems, crystallization and phase and microphase separation are based on two mechanisms: the first, i.e., nucleation and growth, involves the formation of critical nuclei or the presence of heterogeneous nuclei on which growth may occur, and the second, i.e., spinoidal decomposition, involves a small fluctuation in density or composition spread sinusoidally at some characteristic wavelength over the body. In this case, the phases grow at a uniform distance apart in the body.

Annealed plastics tend to be stiffer and more brittle than the unannealed, but this may depend upon the plastic, the fabrication conditions, and the annealing process. Under unfavorable conditions, annealing can be deleterious.

Cooling rates vary with thickness. In general, higher cooling rates can be

used for thin sections, lower rates for thicker ones. Cooling rates for crystalline polymers, polymer blends, and block copolymers are somewhat less critical than for amorphous plastics.

Additives (qv) modify flow and impact resistance and increase uv or oxidative resistance. Performance can be impaired or enhanced as a result of changes in phase or microphase separation, morphology, or residual stress and frozen-in orientation.

Media

The medium affects annealing time. In a liquid medium, short times are required, because the heat transfer is much faster than in air. In addition, a more uniform distribution of temperature is achieved without additional labor cost when the molded part is immediately placed into the bath. Annealing time is, of course, also affected by the thermal properties of the liquid and the annealed article. There are, however, disadvantages to liquid media. Frequently spotting occurs, which cannot be overcome without extra cost. Using oil may present difficulties in handling, and wiping the articles may be required. Although hot air is widely used, immersion in liquid often gives better results. In fact, some plastics, such as nylon and acetal resins, cannot be annealed in hot air because of possible oxidation. These are usually annealed in an oil bath through which an inert gas is bubbled.

A suitable annealing liquid should have an adequate heating range and stability, as well as complete inertness to the annealed plastic. The liquid should also be free of noxious fumes and should not present a fire hazard. Water is a good annealing liquid, but its boiling point is often too low. A small amount of detergent is usually added to promote wetting and rapid draining. For maximum dimensional stability, the liquid bath should have a temperature 25–30°C above the temperature at which the articles are to be used.

Effectiveness

Annealing is a secondary finishing operation that requires time, equipment, energy, and personnel. For maximum effectiveness, conditions should be determined carefully using quality-control methods. A common procedure is to monitor the process in a solvent-induced stress-crazing or stress-cracking test, in which samples are exposed to a liquid or mixture of liquids. The degree of strain or stress needed to cause failure with a given liquid is calibrated with Bergen jigs. However, such tests can only be performed on simple parts. The strip-removal method and determination of the birefringence have also been used. Strip removal was developed in the early 1950s. Its difficulties are created by the need to section samples carefully without modifying the intrinsic stresses imposed by the cutting process and to evaluate the elastic moduli of the skin and core. On the other hand, birefringence measurement is nondestructive and more easily performed, but is currently limited to transparent or translucent materials. Determination

of stress requires a separation of the contribution of the thermal and orientational birefringence (see OPTICAL PROPERTIES; ORIENTATION). Determination of the stress-optical or the stress-fringe coefficient is also required; in some materials, this coefficient is dependent upon the degree of orientation.

Other techniques, such as dsc, sonic modulus, infrared dichroism, fluorescence depolarization, and Brillouin scattering may provide additional data in the future (50,79-87).

Examples

In general, manufacturers of thermoplastics provide recommended annealing procedures. However, because they have little control over the mold design, the processing conditions, the use of regrind, etc, their technical manuals contain a disclaimer. Consequently, data from the technical literature have been chosen for discussion here.

Bisphenol A polycarbonate, developed in the mid 1950s, is an optically clear thermoplastic. In contrast to poly(methyl methacrylate) and polystyrene, it is ductile. However, when annealed below its glass transition, the notched Izod impact strength fell from 854 J/m (16 ft-lb/in.) to 107 J/m (2 ft-lb/in.) for 3-mm samples. Early studies concentrated on possible physical, chemical, and morphological changes. For example, it was found that irradiation causes a decrease in the molecular weight and in the Izod impact strength. Later work demonstrated that annealing increases density, tensile yield stress, flexural yield stress, and glass-transition temperature, but reduces impact strength, elongation, and creep rate (49,85,86). Dynamic mechanical spectra of annealed samples show a small peak just below the glass transition, whereas dsc indicates an excess enthalpy just above the glass transition (56). Fatigue-crack propagation studies on annealed samples indicate a change in effective fracture toughness and that the fatigue properties are strongly affected. The rate at which these properties change depends upon the annealing temperature and the molecular weight of the resin (49,67). More recent studies have centered on residual stresses, shear and dilatational processes, crazing, and the use of fracture mechanics.

Early annealing studies of semicrystalline polymers addressed films in which the degree of crystallinity and the orientation of the crystallites were considered of primary importance. Subsequent work on injection-molded parts of polypropylene, an ethylene-propylene copolymer, and poly(butylene terephthalate) have revealed that complex skin, skewed zone, and core are altered by annealing (3). In the case of poly(butylene terephthalate), the skin was shown to be of lower density, and correspondingly, of lower crystallinity than the core (4). Upon annealing, the skin density increased.

The annealing of polymer blends has not yet been extensively studied. The work on blends of bisphenol A polycarbonate and copolyesters best exemplifies the effects of annealing on a number of properties. It indicates that densification may occur by two different mechanisms: normal densification of a glass and crystallization. The observed degree of crystallization after annealing depends upon the initial blend composition, and the annealing temperature and time; modulus, yield strength, and Izod impact strength are affected (25).

Economic Aspects

Annealing, as a secondary operation adding to the cost of the fabrication of thermoplastic parts, is considered only if there is evidence of part failure caused by residual stress, frozen-in orientation, or objectionable dimensional changes. Every effort should be made by the fabricator to minimize the introduction of excessive stresses and orientation during fabrication through the use of correct mold designs and proper molding conditions. With the development of faster processing equipment, computer controls, and a better understanding of the effects of processing, annealing will continue to play an important role in plastics technology.

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ANTIBODIES AND ANTIGENS. See Supplement.

ANTIBODIES AND ANTIGENS, POLYMER-BOUND

All vertebrates, including humans, are capable of synthesizing antibody molecules that will bind to virtually any disease organism or foreign substance. It is generally agreed that more than 1,000,000 different antibodies can be made, each able to bind specifically to the molecule (antigen) that stimulated its synthesis. Antibodies are large proteins shaped like lobsters with two identical claws. The claw-like domains or binding sites of each antibody type differ in amino acid sequence. This variation in protein structure explains the extraordinary diversity found among antibodies (see Fig. 1).

During the past decade, scientists have learned how to produce large amounts of homogeneous antibodies to order. This is done by altering normal antibody producing cells so they can easily be grown in the laboratory. Cells that produce the desired antibody are selected and grown in culture. Each cell clone produces only one specific antibody, hence such products are termed monoclonal antibodies (1).

Monoclonal antibodies are already used in a wide variety of applications. They are bound to polymeric supports and used to purify molecules of many types.